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**None**

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(54) **A process of ethoxylating a derivative of technical cashew nut shell liquid**

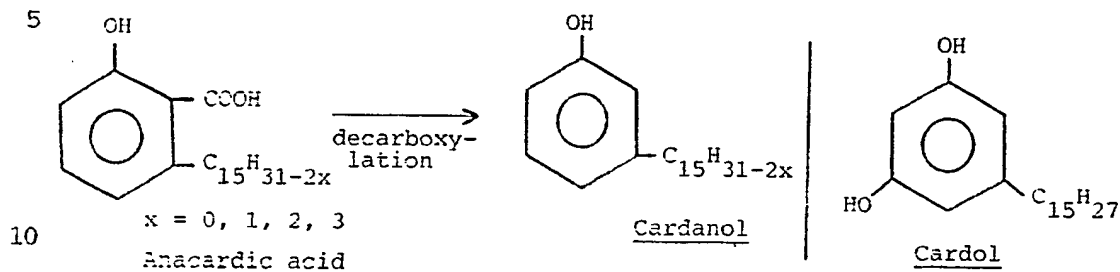
(57) A process for ethoxylating cardanol in which a mixture comprising a predominant amount of cardanol and a relatively small amount of cardanol oligomer is ethoxylated without previously distilling the cardanol or subjecting the mixture to another purification method to remove the oligomer. Preferably, the mixture may be obtained by subjecting technical cashew nut shell liquid to a reaction with formaldehyde together with an amine.

The invention also extends to an ethoxylated mixture of a predominant amount of cardanol and a minor amount of cardanol oligomer, as well as a cleaning composition containing such an ethoxylated mixture.

Title: A process for ethoxylating a derivative of technical cashew nut shell liquid

This invention relates to a process for ethoxylating cardanol.

It is known that technical cashew nut shell liquid (CNSL) contains mainly two components, i.e. cardanol and cardol. Natural CNSL contains mainly anacardic acid which is converted to cardanol by decarboxylation:

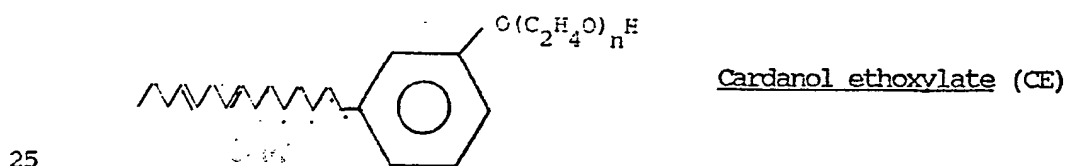


In cardanol the aliphatic side chain is predominantly  $C_{15}H_{27}$  ( $x = 2$ ); the average number of double bonds is 1.8.

Cardanol can be prepared in several ways:

15 According to Indian patent 111326 cardanol is obtained by distillation of cashew nut shell liquid. In example 4 of this Indian patent ethylene oxide is reacted with cardanol, whereby the cardanol is ethoxylated.

When cardanol is ethoxylated with ethylene oxide, a compound having the 20 formula  $C_{15}H_{31-2x}C_6H_4O(C_2H_4O)_nH$  is obtained. For  $x = 2$ :



Said Indian patent discloses that the cardanol ethoxylates are suitable as emulsifiers, detergents, dispersants, etc.

In "Fette, Seifen, Anstrichmittel", 77:197-199, 1975, cardanol is obtained by fractionation of commercial CNSL (cardanol distilled at 30  $204^\circ C/1.0$  mmHg). The cardanol obtained was used for the preparation of ethylene oxide adducts of cardanol, which adducts are reported to have surface-active properties.

The disadvantages of vacuum distillation of CNSL to obtain cardanol are that i) polymerization of all components of the CNSL, including 35 cardanol, tend to occur and ii) the tendency of cardanol and cardol to co-distil.

Molecular distillation also leads to the above polymerisation and

moreover requires expensive equipment.

GB 2,152,925 relates to a method of separating cardanol from mixtures containing cardanol and dihydric phenols such as cardol, and in particular from CNSL which contains mainly cardanol and cardol. According to said British patent the mixture is reacted with formaldehyde and a primary or secondary amine (Mannich reaction) or a dilute mineral acid, whereby the dihydric phenols in the mixture form a high molecular weight reaction product, while the monohydric cardanol remains unreacted. After working-up the cardanol is then subjected to vacuum distillation.

GB 2,066,820 discloses treating technical CNSL with an amine so that the dihydric cardol forms an amine salt in preference to cardanol. Thereafter the cardanol is subjected to vacuum distillation.

In the cardanol product obtained according to the two above mentioned British patents but prior to the distillation step, the cardanol is still contaminated with oligomeric product, which is mainly cardanol dimer as appeared from applicant's gel permeation chromatography (GPC) data.

In a gel-permeation chromatogram from cardanol obtained according to GB 2,152,925 employing the Mannich reaction, a peak A represented cardanol and peak B represented the dimer; a material of the latter peak showed a molecular weight exactly twice the molecular weight of the material from peak A, the monomeric cardanol. After distillation the dimer peak disappeared.

The oligomeric component is also suggested in the prior art, i.e. in an article by J.H.P. Tyman et al in Journal of Chromatography, 213 (1981) 287-300, in particular pages 297-299, wherein dimeric and trimeric products are reported to be present in purified cardanol,

Surprisingly, it was found that ethoxylation of a mixture comprising a predominant amount of cardanol and a relatively small amount of cardanol oligomer, without previously distilling the cardanol or subjecting the mixture to another purification method to remove the oligomer, yields an ethoxylation product exhibiting substantially the same viscosity (both in water and in neat condition) as the ethoxylation product of distilled cardanol, the latter product having been obtained under the same conditions.

The product obtained with undistilled cardanol has the same useful properties as the product obtained with distilled cardanol, in particular in cleaning compositions wherein cardanol ethoxylate also serves as

a viscosity builder.

The above means that not only the cardanol but also the oligomer is ethoxylated in the reaction with ethylene oxide (which conclusion can already be drawn from the fact that no water-insoluble material remains 5 after the same amount of ethylene oxide has been added as in the reaction with the same amount of pure cardanol).

The cardanol dimer, which is the principal constituent of the oligomeric product, is formed during the decarboxylation under acid conditions and therefore is believed to have an ether structure because under 10 these conditions the two OH groups of the cardanol will react to form the dimer.

It is surprising that in spite of the absence of a free OH group in the dimer, this molecule is capable of being ethoxylated. Furthermore, the above discussed literature teaches away from the use of undis- 15 tilled cardanol.

Furthermore, the GPC data for the molecular weight distribution show that the oligomers remain intact during ethoxylation: pure cardanol as obtained according to the Mannich reaction plus distillation carried out as described hereinafter in the experimental part of the present description, was ethoxylated to an n value of 13 (i.e. 13 moles of ethylene oxide per mole of cardanol) as also described hereinafter in the experimental part; this ethoxylation was repeated for cardanol obtained with the same Mannich reaction, however without distillation. The molecular weight distributions were clearly different. Had the oligomer not 25 remained intact during ethoxylation, i.e. split into the monomeric molecules, then the distributions would have been identical.

#### Example 1

A) In a vessel, equipped with a stirrer, the following ingredients were added under constant stirring in the order shown: 30 kg of technical 30 cal CNSL, 74 kg of methanol, 1.2 kg of diethylene triamine (DETA) and 10 kg of 40% formaldehyde. A slightly exothermic reaction took place; the temperature did not exceed 30°C. The mixture was allowed to stand for 1-1½ hours, during which period phase separation took place. The upper phase was a slightly reddish solution, the lower phase solidified 35 and had a dark colour.

The upper phase (which contained cardanol as well as methanol) was siphoned into large containers (25 l, with caps). The lower phase polymer remained in the vessel.

Into each 25 l container the following materials were added: 15 kg of

upper phase, 3.5 kg of brine solution and 1.8 kg of petroleum spirit (40/60). Then the containers were shaken several times and allowed to stand for 2-3 hours, allowing separation of the dark upper layer (cardanol plus solvent). Regular tapping of the vessel was required to aid separation in the initial stage. The dark upper layer of cardanol plus solvent was carefully siphoned into a large separating funnel to facilitate an easier separation.

Solvent removal was carried under vacuum in a rotary evaporator. The temperature was maintained below 55°C. The solvent was collected in a nitrogen trap. From 30 kg of CNSL about 18 kg of cardanol (also containing oligomer) was obtained.

- B) The cardanol obtained in step A) was subjected to vacuum distillation at a pressure of 0.55 mmHg and a temperature of 180-190°C. From 18 kg of cardanol + oligomer 11.4 kg of pure cardanol was obtained.
- 15 C) Cardanol ethoxylate containing 13 moles of ethylene oxide (cardanol 13 EO) was prepared as follows:

A 5 l autoclave, fitted with a water-cooled stirrer, condenser, thermometer and gas dispersion thimble was connected through two 1 litre safety bottles to a graduated cylinder containing white oil and a manifold connected to low-pressure nitrogen and a tank of ethylene oxide.

906 g (3 g moles) of cardanol was charged to the autoclave followed by 2 g of powdered sodium hydroxide. The autoclave thermometer, gas disperser and contents were weighed. A slow stream of nitrogen was started through the alcohol and the temperature raised to 150-160°C by means of a heating mantle. Ethylene oxide gas was admitted to the manifold and allowed to escape momentarily to the atmosphere through a three-way stopcock. This stopcock was then turned to vent the nitrogen to the atmosphere and the ethylene oxide was simultaneously introduced into the flask.

30 The white oil in the graduated flask allowed a small hydrostatic head to build up (about 2.5 cm Hg), and the ethylene oxide rate was increased to the point where an occasional bubble of ethylene oxide escaped.

The absorption of ethylene oxide into the cardanol was immediate and the temperature was allowed to rise to 180-220°C. It was held there during the course of the reaction until the required weight of ethylene oxide had been absorbed. In the present case (cardanol 13 EO) this weight was 1.716 g.

In shutting down, the apparatus was completely purged using nitro-

gen and then re-weighed. The free alkali is then neutralised with acetic acid to a phenolphthalein end-point (external indicator).

The value for  $n (= 13)$  was confirmed by measuring the average mole weight by "Supercritical Fluid Chromatography" (D.W. Later et al, Laboratory, August 1986, page 108; and P.R. Geissler, JAOCS., 66 (1989) 685).

In the same way as described above, using the same amount of cardanol as starting material, the following cardanol ethoxylates were prepared:

- 10 Cardanol 3 EO: weight absorbed ethylene oxide 396 g  
 Cardanol 8 EO: weight absorbed ethylene oxide 1,056 g

The obtained products gave the following results in terms of the viscosity:

TABLE 1

15	Viscosity at 30°C	
	5% solution in H <sub>2</sub> O    neat	
a) Ethoxylated undistilled		
cardanol + oligomers 13 EO	15 mPas	470 mPas
b) Ethoxylated distilled cardanol		
20    (without oligomer) 13 EO	15 mPas	450 mPas

Applicant's Dutch patent application 9100944, filed 31st May, 1991, discloses that certain combinations of cardanol ethoxylation products having different values for  $n$ , the number of EO units, show a synergistic increase in the viscosity in aqueous compositions in which they are incorporated, compared to the single cardanol ethoxylation products.

The following table 2 shows the viscosities at 30°C for a number of combinations of cardanol ethoxylation products having different  $n$  values in water and compares products containing cardanol ethoxylate prepared from the above undistilled cardanol (a) and from the above distilled cardanol.

TABLE 2

	HLB Combination	"n" Combination	Viscosity, 30°C
a) CE + oligomer	6.8/13.5	3/13	1130 mPas
b) CE	6.8/13.5	3/13	1250 mPas

Weight ratio cardanol ethoxylates having different  
n values 1:4; total solids in aqueous composition 10%

	HLB Combination	"n" Combination	Viscosity, 30°C
a) CE + oligomer	11.3/13.5	8/13	14,000 mPas
b) CE	11.3/13.5	8/13	14,500 mPas

Weight ratio cardanol ethoxylates having different  
n values 1:4; total solids in aqueous compositions 10%

	HLB Combination	"n" Combination	Viscosity, 30°C
a) CE + oligomer	11.3/13.5	8/13	1100 mPas
b) CE	11.3/13.5	8/13	1050 mPas

Weight ratio cardanol ethoxylates having different  
n values 1:2; total solids in aqueous composition 7%

CLAIMS

1. A process for ethoxylating cardanol in which a mixture comprising a predominant amount of cardanol and a relatively small amount of cardanol oligomer is ethoxylated without previously distilling the cardanol or subjecting the mixture to another purification method to remove the oligomer.
2. A process according to claim 1, in which mixture is obtained by subjecting technical cashew nut shell liquid to a reaction with formaldehyde together with an amine.
3. An ethylated mixture of a predominant amount of cardanol and a minor amount of cardanol oligomer.
4. A cleaning composition containing an ethoxylated mixture as claimed in claim 3.
5. A process of ethoxylating cardanol mixture with cardanol oligomer substantially as hereinbefore specifically described with particular reference to the Examples.



**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**

Application number

GB 9126845.8

<b>Relevant Technical fields</b> (i) UK Cl (Edition 1) C2C(W5) ; C3R(R27KRF) (ii) Int Cl (Edition 5) C07C 43/23	<b>Search Examiner</b>  S I AHMAD
<b>Databases (see over)</b> (i) UK Patent Office (ii) ONLINE DATABASE: CAS-ON-LINE AND WPI	<b>Date of Search</b>  5 FEBRUARY 1993

Documents considered relevant following a search in respect of claims 1-5

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	None	

Category	Identity of document and relevant passages	Relevant to claim(s)

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